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Effects of heat treatment on the mechanical properties and corrosion behaviour of the Mg-2Zn-0.2Mn-xNd alloys

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ABSTRACT

The selected-dissolution behaviour of metals after the film rupture determines the propagation of localized corrosion. Meanwhile, excessive Cl^- aggregations and too fast resorption behaviour may prematurely lead to the loss of mechanical properties. In this study, the degradation behaviour and mechanical properties of the heat-treated Mg-2Zn-0.2Mn-xNd (MZM-xNd) in the simulated body fluid were analyzed using XRD, XPS, FT-IR, TEM, 3D/CLSM and AFM/SKPFM. Besides, the film formation and rupture mechanism were illuminated through the spectroscopic analysis, and its role on the propagation of localized corrosion was also discussed. The results demonstrate that the localized corrosion propagates inside the matrix (underneath the surface film layers) and exhibits a filiform-like corrosion morphology. Immersion and polarization tests together with morphology observations indicate that the MZM-0.6Nd has the moderate degradation rate by giving rise to the densification of the film layer, with the corrosion rate of 0.83 mm/y. However, the corrosion rate progressively increased (1.83 mm/y, 3.08 mm/y), as the Nd content increased (1.22%, 1.88%), due to the more large-size phases present in the matrix. It will exacerbate the corrosion resistance by facilitating the localized dissolution of the degradation layers, enhancing the adsorption for Cl^- and promoting the mass transport, thereby retarding the self-healing capability and the occurrence of the localized corrosion. The significant improvement in mechanical strength of MZM-0.6Nd, with the ultimate tensile strength and elongation of 224 MPa and 19.2%, making it appear the ductile fracture feature with small dimples. It was attributed to the role of interactions with the fine-grained microstructure, the pinning dislocations, and the strengthening phases dispersedly distributed in the matrix.

1. Introduction

Because of its low corrosion potentials, magnesium and its alloys easily dissolve in aqueous solutions, particularly in those containing chloride ion electrolytes. Making use of the corrosion properties of Mg alloys, in recent years, the development of the Mg matrix degradation implant materials has received great attention [1–4]. Another advantage of Mg in relation to elastic modulus is close to that of the human bone, which can effectively minimize the stress-shielding effect and induce the new bone formation. Additionally, the release of Mg^{2+} can offer the possibility of better physiological repair and better reconstruction of vascular compliance [2]. Unfortunately, the inherent poor corrosion resistance of the Mg-based implants and the attack of aggressive ions under the physiological conditions (7.4–7.6) give rise to fast degradation rates and hence, the materials will lose the mechanical integrity before the tissues have sufficient time to heal. As a result, how to explore the key factors affecting corrosion and further improve the mechanical and corrosion properties is of great value.

To date, some efforts have been paid to address these issues, such as composites [8–10], developing the processing methods [5,11–13], surface modification and micro-alloying [6,7,14–19]. Among all the methods, alloying is an effective approach not only can enhance the corrosion resistance with the microstructure modification, but also endows the alloys with the moderate mechanical properties, tailoring the phase sizes, and grain sizes along the matrix. The maximum solubility of Nd in Mg (HCP) is approximately 3.6 wt% at 552 °C. When the temperature is below 200 °C, the solubility drops rapidly to near zero, which provides a strong potential of age hardening. Futhermore, the addition of Nd in the

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Mg alloys can enhance the room temperature and elevated temperature formability through the texture weakening [6]. Moreover, the significant improvement of the cell viability and biocompatibility have been detected in the Mg-Nd-Zn-Zr [20,21]. Therefore, most of Nd-containing alloys have gained the great attention. Mingo et al. [22] reported the microstructure and corrosion behaviour of the Mg-9Al alloy with the minor alloying addition (Mn, Y, Nd, Ca, and Sn). It revealed that all the alloying elements, except Sn, reduced the difference in Volta potentials between the phases and the matrix. Hong et al. [23], Su, et al. [24], and Liu et al. [25] separately studied the phase stability and its effect on the electrochemical-corrosion behaviour of ZK40, Mg-4Al-4Nd-0.2Mn and Mg-5Al-0.4Mn-xNd (x = 0, 1, 2 and 4) in the NaCl solution, respectively. Zhang et al. [26,27] and other studies [28–30] further investigated the effects of double extrusion and Ag addition on the degradation behaviour and corrosion products features of Mg-2.25Nd-0.11Zn-0.43Zr, Mg-2.70Nd-0.20Zn-0.41Zr and Mg-3Nd-0.2Zn-0.4Zr-xAg (x = 0, 0.2, 0.4, and 0.8) alloys in the Hank's solution. In addition, the mechanical, corrosion properties, and biocompatibility of degradable extruded Mg-Nd-Zn-Zr alloys in vitro and in vivo were also investigated by Zhang et al. [31], Shi et al. [32] and Qin et al. [33]. In view of the above considerations, the biodegradable MZM-xNd alloys were designed and prepared. Therein, Zn, Nd, and Mn were essential nutrient elements in the human body. Zn is also recognized as a highly essential element for humans. In the absence of zinc, almost all physiological functions are strongly disturbed. Mn plays a primary role in the activation of multiple enzyme systems and has no toxic effect except after extreme occupational exposure. Besides, the beneficial effects of the Mn addition on the corrosion biodegradable Mg-4Zn-0.5Ca alloy was reported by Dae et al. [33], in which the dense films of MnO and MnO_2 on the surface can inhibit the chloride ion permeation and control the matrix dissolution. However, the effects of the phase characteristic and the film layer with the incorporation of Nd of the heat-treated MZM-xNd in simulated body fluid (Kokubo) were scarcely reported to now.

In this study, the microstructure, mechanical and degradable behaviour of the heat-treated MZM-xNd alloys were analyzed using TEM, AFM, FT-IR, XPS and 3D/CLSM. Combined spectroscopic analysis for the film formation mechanism and its role on the initiation and propagation of the localized corrosion were also discussed. Besides, the Gibbs free energy of the film layer with Nd modification has been analyzed.

2. Experimental materials and methods

2.1. Materials preparation

The studied alloys with the nominal composition of Mg-2Zn-0.2Mn-xNd (x = 0, 0.6, 1.2, 1.8) were fabricated with high-purity Mg (99.94%), high-purity Zn (99.99%), Mg-5Mn (99.81%) and Mg-25Nd (99.87%) master alloys. They were received from Global Jinxin International Technology Co., Ltd, Beijing, China. All compositions are in wt.% as default. The entire process of mixing, melting, and casting was performed in the ZG-2 vacuum induction melting furnace under the (Ar + 2% SF_6) atmosphere. The melt was kept at 750 °C for 5 min, and then poured into a cylinder-shaped graphite mould for natural cooling in the air. Compositions were analyzed using ICP-AES (Varian 715-ES), and the results were given in Table 1. Afterwards, all samples were subjected at the 420 °C treatment for 24 h and then cooled by water.

2.2. Microstructure observations and mechanical tests

For the microstructure observations, samples were ground with SiC papers from 800 up to 5000 grits. Then, they were mechanically polished with the diamond down to 0.25 μm in order to obtain a mirror-like surface, followed by ethanol washing and drying. Subsequently, they were etched using the picric acid solutions for 50 s to reveal the microstructure. Microstructure observations were examined by optical microscopy (Leica, DM2500-M), electron probe micro-analyzer (EPMA, JXA-8100) and scanning electron microscopy together with energy dispersive spectroscopy (SEM, Zeiss Auriga). Phase identification was conducted using TEM (TECNAI G2) and XRD (SmartLab), with the scan rate of 1°/min.

Table 1
Chemical composition of the heat-treated Mg-2Zn-0.2Mn-xNd alloys (wt.%).

Alloys	Mg	Zn	Nd	Mn	Cu	Fe	Ni
Mg-2Zn-0.2Mn	Bal.	2.12	/	0.20	<0.01	<0.01	<0.01
Mg-2Zn-0.2Mn-0.6Nd	Bal.	2.08	0.62	0.20	<0.01	<0.01	<0.01
Mg-2Zn-0.2Mn-1.2Nd	Bal.	2.06	1.22	0.20	<0.01	<0.01	<0.01
Mg-2Zn-0.2Mn-1.8Nd	Bal.	2.18	1.88	0.20	<0.01	<0.01	<0.01

The relative Volta potential distributions between the Mg matrix and second phase were detected by atomic force microscope (AFM, MFP 3D Infinity) in a tapping model (SKPFM) [15]. Prior to the SKPFM tests, the specimens with the dimensions of 8 × 8 × 2 mm were finally polished down to 0.25 μm, and then the tests were carried out immediately. Mechanical properties at room temperature were measured by a universal testing machine (CM 75105) at a tensile speed of 1 mm/min. Besides, an extension meter with a gauge length of 10 mm was used to measure the elongation. Four duplicate specimens were tested for each alloy and the values were averaged in order to assure the accurate tensile properties.

2.3. Corrosion measurements

A conventional three-electrode electrochemical configuration was employed using a flat cell (Princeton Versa STAT) with 1 cm^2 WE exposed to the quiescent Kokubo solution. A saturated calomel electrode (SCE) and Pt-mesh counter electrode were used. Prior to polarization tests, samples were conditioned at the open circuit potentials (OCP) for 10 min to obtain a stable potential. Polarization tests were done with a scanning rate of 1 mV/s, and the corrosion parameters such as corrosion potentials (vs. E_{ocp}) and current density (J_{corr}, A/cm^2) were obtained via Tafel-type fitting. Faraday's law was used to convert the obtained current densities into corrosion rates (CR) according to the following equations [34]:

$$CR = K_1 \times EW \times J_{corr}/\rho \quad (1)$$

$$EW = 1 \Big/ \sum (f_i n_i / W_i) \quad (2)$$

where the CR is the corrosion rate (mm/year), EW is the alloy equivalent weight, which is dimensionless, $K_1 = 3.27 \times 10^{-3}$ mm g $\mu A^{-1} cm^{-1} year^{-1}$, J_{corr} is the corrosion current density (μA/cm^2), and ρ is the density (g/cm^3). The f_i and n_i were the mass fraction and atomic weight, respectively. The W_i is the valence of each element in the alloy. Besides, the electrochemical impedance spectroscopy (EIS) was conducted on MZM-xNd alloys over the frequency range of 100 kHz to 10 mHz. The EIS spectra were fitted using the ZSimpWin 3.10 software. In all cases, at least four tests for each electrochemical test were performed to ensure reproducibility.

In accordance with ASTM G31-72 [35], the MZM-xNd alloys were immersed in the Kokubo solution for 10 days at 37 ± 0.5 °C. The chemical composition of the Kokubo's solution was listed in Table 2. Before the immersion tests, the specimens were prepared in the form of Φ 18 mm × 2 mm and mechanically ground with